

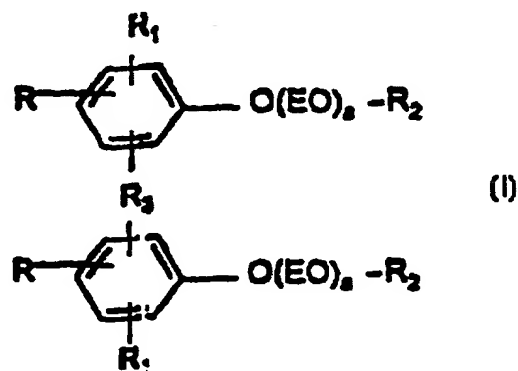


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(54) Title: ANIONIC SURFACTANTS HAVING MULTIPLE HYDROPHOBIC AND HYDROPHILIC GROUPS**(57) Abstract**

Mild and environmentally benign bis-alkylphenol alkoxyated gemini surfactants of formula (I), wherein R independently represents alkyl, R₁ independently represents hydrogen of alkyl, R₂ independently represents -SO₃M, -P(O)(OM)₂, -CH₂COOM, -CH₂CHOHCH₂SO₃M, wherein M represents alkali or alkaline earth metal, ammonium or an organic base salt; R₃ represents alkylene of from one to about 10 carbon atoms or -C(O)-R₄-C(O)- wherein R₄ represents alkylene or aryl, and -O-R₅-O-, wherein R₅ represents aliphatic or aromatic moieties; EO represents ethyleneoxy; and a ranges from zero to about 100.



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ANIONIC SURFACTANTS HAVING MULTIPLE
HYDROPHOBIC AND HYDROPHILIC GROUPS

5

This invention relates to a novel group of anionic surfactants having at least two hydrophobic moieties and at least two hydrophilic groups per molecule.

10

BACKGROUND OF THE INVENTION

Anionic surfactants carry a negative charge on the hydrophilic portion, usually in the form of a carboxylate, phosphate, sulfate or sulfonate. These surfactants find
15 use in emulsion polymerization as well as in agricultural chemicals, personal care and household products, industrial and institutional cleaners. They function as emulsifiers, cleaners, wetting agents, foaming and frothing agents such as for shampoos, car washes, carpet
20 shampoos, hand dishwashing, latex foaming, oil recovery and other industrial uses.

While surfactants generally have one hydrophilic group and one hydrophobic moiety, recently a group of compounds having two hydrophobic moieties and two
25 hydrophilic groups have been introduced. These have become known as "Gemini surfactants" in the literature

(Chemtech, March 1993, pp 30 - 33), and J. American Chemical Soc., 115, 10083-10090, (1993) and the references cited therein. Other surfactant compounds having two hydrophilic groups and two hydrophobic moieties have been disclosed but not referred to as Gemini surfactants.

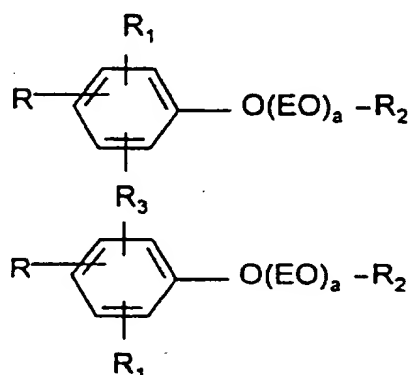
It is known to sulfate, phosphate and carboxylate surfactants through functionalization of the hydroxyls.

However, secondary hydroxyl's undergo sulfation, phosphorylation or carboxylation poorly, leading to undesired by-products and/or high levels of acid or low product yields. The compounds of the invention contain primary hydroxyl groups which can be more efficiently functionalized.

There is also a need for new and more effective and efficient surfactants, as well as the need for mild surfactants which are biologically compatible in an ecologically sensitive environment. A new class of compounds has been developed which demonstrates improved surface-active properties that are further characterized as mild, and environmentally benign.

SUMMARY OF THE INVENTION

According to the invention, an improved class of anionic surfactants have been provided comprising
 5 compounds of the formula:



10 wherein R independently represents alkyl of from about 4 to about 20 carbon atoms, R_1 independently represents hydrogen and alkyl of from about 4 to 20 carbon atoms; R_2 independently represents $-\text{SO}_3\text{M}$, $-\text{P}(\text{O})(\text{OM})_2$, $-\text{CH}_2\text{COOM}$,
 15 $-\text{CH}_2\text{CHOHCH}_2\text{SO}_3\text{M}$, wherein M is hydrogen, alkali metal such as sodium, potassium, ammonium or organic base salt; and R_3 represents alkylene of from one to about 10 carbon preferably from about 1 to about 4 atoms or $-\text{C}(\text{O})-\text{R}_4-\text{C}(\text{O})-$ wherein R_4 represents alkylene of from 1 to about 10 carbon
 20 atoms and aryl, e.g. phenylene. R_3 also represents $-\text{O}-\text{R}_5-\text{O}-$ wherein R_5 represents aliphatic or aromatic moieties of

from 1 to about 10 carbon atoms. EO represents ethyleneoxy radicals, a is a number of from 0 to about 100 preferably one from about 0 to about 30. Preferably, R₃ is alkylene and more preferably -CH₂. As used herein the
5 terms "alkyl" or "alkylene" include straight as well as branched chains.

When compared to the corresponding conventional anionic surfactants, the novel compounds of the present invention show two unexpected surface active properties;
10 unusually low critical micelle concentration (CMC) showing exceptional surfactant effectiveness and pC₂₀ values that exhibit exceptional surfactant efficiency in aqueous media. These properties are a measure of the tendency of the surfactant to form micelles and adsorb at the
15 interface respectfully, and consequently, to reduce surface tension.

Preferably, R is alkyl of from about 6 to about 10 carbon atoms, and R₁ is preferably hydrogen. The organic base salts of the compounds of the invention can be
20 illustrated by monoethanolamine, diethanolamine, triethanolamine, triethylamine, trimethylamine,

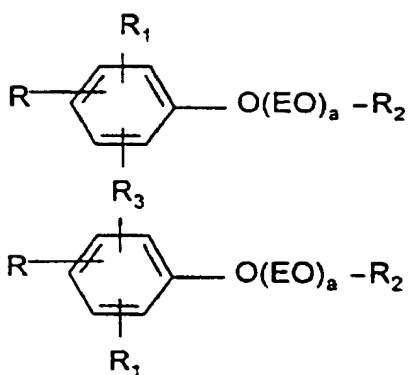
N-hydroxyethyl morpholine and the like.

More specifically, the compounds of the present invention comprise:

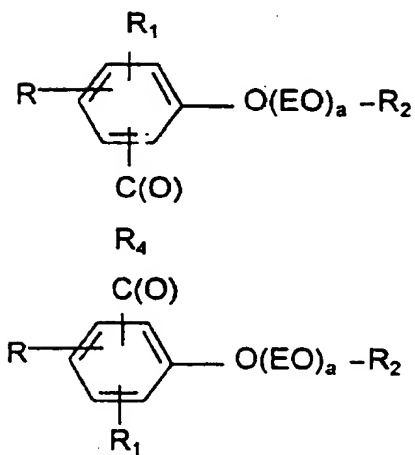
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II.

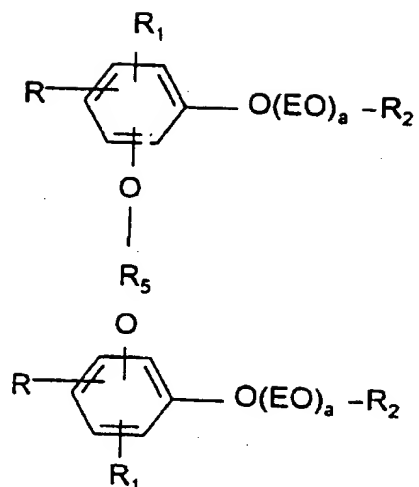
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10 III.



IV.



5 wherein R, R₁, R₂, R₄, a, and R₅ are as defined hereinbefore.
 R₃ represents alkylene, preferably methylene. It is noted
 that when R₂ is hydrogen or capped according to procedures
 well known in the art for preparing alkoxyated nonionic
 10 surfactants, the compounds are nonionic and are, although
 considered as included in the generic invention, they
 would be claimable as separate and distinct species.
 Compounds which are nonalkoxyated have been found to be
 particularly effective in blends such as with silicone
 15 compounds.

The primary hydroxyl group of the nonionic
 surfactants of this invention can be readily phosphated,
 sulfonated or carboxylated by standard techniques.

In addition to new compounds, the invention also discloses novel synergistic compositions when the compounds of the invention are blended with other surfactants.

5

DETAILED DESCRIPTION OF THE INVENTION

The compounds of the invention can be prepared by a variety of synthetic routes. The compounds of Formula II
10 can be prepared by condensing a monoalkyl phenol with paraformaldehyde in the presence of an acid catalyst such as acetic acid. The compounds of Formula III can be synthesized by a Lewis acid catalyzed reaction of an alkylphenol with a dicarboxylic acid, e.g., terephthalic
15 acid or succinic acid. The compounds of Formula IV can be synthesized by a base catalyzed reaction of an alkyldihydroxybenzene with a dibromide.

These products can be oxyalkylated by reacting the product with an alkylene oxide according to known methods,
20 preferably in the presence of an alkaline catalyst. The free hydroxyl groups of the phenol or the alkoxylated derivative can then be sulfated, phosphated or carboxymethylated using normal methods such as sulfation with sulfamic acid or chlorosulfonic acid or sulfur
25 trioxide, or carboxymethylated with an acylating agent such as a chloroacetic acid.

For alkylation conditions and commonly used alkylating agents, see Amphoteric Surfactants Vol. 12, Ed. B.R. Bluestein and C.L. Hilton, Surfactant Science Series 1982, pg. 17 and references cited therein, the disclosures
5 of which are incorporated herein by reference.

For sulfation and phosphorylation, the reaction product of the paraformaldehyde and the phenol can be reacted with a sulfating or phosphorylating agent such as sulfur trioxide, sulfamic acid, chlorosulfonic acid or phosphoric anhydride
10 to form the compounds of the invention (Sulfation techniques are discussed in Surfactant Science Series, Vol 7, Part 1, S. Shore & D. Berger, page 135, the disclosure of which is incorporated herein by reference. For phosphorylation review see Surfactant Science Series, Vol 7,
15 Part II, E. Jungermann & H. Silbrtman, page 495, the disclosure of which is incorporated herein by reference.)

Since the surfactants of the invention exhibit an extremely low critical micelle concentration (CMC) as compared with conventional surface-active agents because
20 of the presence of two hydrophobic moieties and two hydrophilic groups in their molecule and since they are able to fully reduce surface tension and are highly soluble in water, the surfactants of the invention are extremely effective in aqueous solution at low
25 concentrations. The surfactants of the invention can be used in any amount needed for a particular application

which can be easily determined by a skilled artisan without undue experimentation.

The surfactants of the invention can be used alone as the essential hydrotrope component.

5 It has been unexpectedly found that blends of the compounds of the invention with certain conventional well known anionic, nonionic, cationic and amphoteric surfactants provide synergistic effects in relation to critical micelle concentration and surface tension
10 reducing ability.

 Examples of the nonionic surfactants usable herein include fatty acid glycerine and polyglycerine esters, sorbitan sucrose fatty acid esters, higher alcohol ethylene oxide adducts, polyoxyethylene alkyl and alkyl
15 allyl ethers, polyoxyethylene lanolin alcohol, glycerine and polyoxyethylene glycerine fatty acid esters, polyoxyethylene propylene glycol and sorbitol fatty acid esters, polyoxyethylene lanolin, castor oil or hardened castor oil derivatives, polyoxyethylene fatty acid amides,
20 polyoxyethylene alkyl amines, an alkylpyrrolidone, glucamides, alkylpolyglucosides, mono- and dialkanol amides. Examples of the anionic surfactants used herein include fatty acid soaps, ether carboxylic acids and salts thereof, alkane sulfonate salts, α -olefin sulfonate salts,
25 sulfonate salts of higher fatty acid esters, higher alcohol sulfate ester or ether ester salts, higher alcohol

phosphate ester and ether ester salts, condensates of higher fatty acids and amino acids, and collagen hydrolysate derivatives.

5 Examples of the cationic surfactants used herein include alkyltrimethylammonium salts, dialkyldimethylammonium salts, alkyldimethylbenzylammonium salts, alkyipyridinium salts, alkylisoquinolinium salts, benzethonium chloride, and acylamino acid type cationic surfactants.

10 Examples of the amphoteric surfactants used herein include amino acid, betaine, sultaine, phosphobetaines, imidazoline type amphoteric surfactants, soybean phospholipid, and yolk lecithin.

15 Any of commonly used auxiliary additives such as inorganic salts such as Glauber salt and common salt, builders, humectants, solubilizing agents, UV absorbers, softeners, chelating agents, and viscosity modifiers may be added to the surfactants of the invention or blends thereof with other surfactants as disclosed herein.

20 The anionic surfactants of the invention are extremely mild and non-irritating to both eyes and skin and exhibit low toxicity; exhibit enhanced wetting speed, greater surface tension reduction, high foaming and foam stabilization properties, and excellent compatibility with
25 other surfactants. The products of the invention are stable over a wide pH range and are biodegradable. These

properties make these surfactants adaptable for use in products ranging from cosmetics to industrial applications, such as for non-irritating shampoos, e.g., baby shampoos, body shampoos, bubble baths, bar soaps, bath gels, hair conditioning gels, lotions, skin creams, make up removal creams, liquid detergents, and other washing and cosmetic products that contact the skin. The surfactants of the invention can also find use as hard surface cleaners including cars, dishes, toilets, floors, and the like; laundry detergents and soaps, metal working aids and the like.

It has also been unexpectedly found that the compounds of the invention particularly nonalkoxylated compounds are particularly useful in novel superwetting compositions containing an organosilicone compound(s) which can be represented by the general formula:

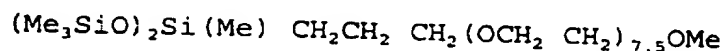
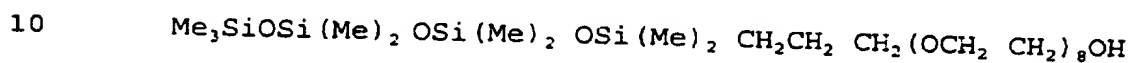
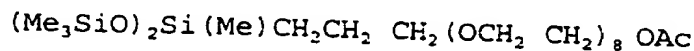
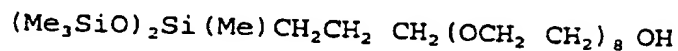


Formula V

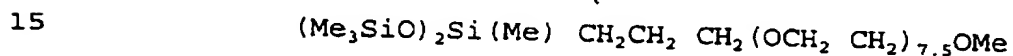
wherein M represents $Me_3SiO_{1/2}$ (represents Me_3SiO or Me_3Si as necessary to form a chemically complete structure); D represents Me_2SiO ; D' represents $MeRSiO$; Me equals CH_3 ; R equals $C_nH_{2n}O(C_2H_4O)_a(C_3H_6O)_bR'$; y ranges from about 0 to 5, preferably zero; x ranges from about 1 to 5, preferably 1; n ranges from about 2 to 4, preferably 3; a ranges from about 3 to 25, preferably 3 to 15; and b ranges from about 0 to 25, preferably 0 to 15; it being understood that the oxyalkylene groups may be random and/or block mixtures;

and R' can be hydrogen, an alkyl group having 1 to 4 carbon atoms, or an alkyl ester group wherein the alkyl group of the ester has 1 to 4 carbon atoms. Each R' can be same or different on any given molecule. Preferably,
 5 R' is hydrogen or a methyl group.

These organosilicone compounds can be represented by the following examples:



The most preferred organosilicone compound is represented by the following formula:



also known as SILWET L-77.

This is more fully disclosed in copending U.S. patent application Serial No. 08/576,749, of Gao, et al., filed on even date herewith the present application, the entire
 20 disclosure of which is incorporated herein by reference.

Examples of the present invention are given below by way of illustration and not by way of limitation. All parts and percents are by weight unless otherwise stated.

EXAMPLE I

Preparation of 2,2' methylenebis [4(1,1,3,3-
5 tetramethylbutyl) phenol].

Dissolve 4-(1,1,3,3- tetramethylbutyl phenol [724 g.
3.51 mole] in a minimum amount of xylene at room
temperature in a three necked round bottom flask. Para-
formaldehyde (15 g. 0.5 mol) and glacial acetic acid (100
10 mL.) were added slowly to the solution under argon.
Reaction temperature was slowly raised to 135°C (about
150°C external temperature) as the solution was stirred
vigorously. Water generated during the reaction was
collected by Dean-Stark apparatus. After stirring 5
15 hours at 135°C, GC analysis indicated complete reaction.

The reaction was stopped by distilling out all starting
materials under reduced pressure at 150°C. The final
pure product was obtained by washing the crude product
twice with hexane in the flask. The white solid product
20 was collected by filtration. Melting point of the final
compound is 153°C. The NMR agreed with the structure.
Lit. M.P. 152 - 153°C (Brit J. Pharmacol, 10, 73 - 86
(1955)).

Also prepared according to the method of example I
25 were:

- a) 2,2' methylenebis (4-nonylphenol) was prepared in a similar manner by replacement of the 1,1,3,3,-Tetramethylbutylphenol by 4-nonylphenol in the same mole ratio to formaldehyde.
- 5 b) 2,2' methylenebis (4-dodecylphenol) was prepared by replacing 1,1,3,3-Tetramethylbutylphenol with 4-dodecylphenol at the same mole ratio.
- c) 2,2' methylenebis [4,6-di(1,1-dimethylpropyl) phenol] was prepared by replacing 1,1,3,3-Tetramethylbutylphenol with 2,4-di(1,1-dimethylpropyl) phenol at the same mole ratio (see U.S.2,675,366).
- 10

EXAMPLE II

15

Preparation of 2,2' methylenebis [4(1,1,3,3-tetramethylbutyl) phenol] ethoxylate:

Potassium hydroxide flakes (0.545 g) were added to a melted methylene bisoctylphenol (436 g) in a tarred beaker under nitrogen. Once the KOH was dissolved in it the solution was carefully poured into a preheated 7.57 (2 gallon) reactor. The reactor was degassed by pulling vacuum releasing with Nitrogen. Ethylene oxide (2 - 3 moles) was quickly added allowing for reaction kick. The remaining ethylene oxide (a total of 880 g) was added at 150 - 160°C and 90 psig max. After 30 minutes the

20

25

pressure remained constant, the reaction was cooled to 120°C and vacuum stripped with slight nitrogen sparge for 20 minutes. Finally acetic acid was added to a pH of 7 to neutralize KOH. Analysis by NMR indicated 20 moles
5 ethylene oxide had reacted. Cloud point (1% aqueous) was 68°C.

The following ethoxylates were prepared according to the method of Example II.

- a) 2,2' methylenebis [4-(1,1,3,3-
10 Tetramethylbutyl)phenol] 2EO was prepared in a similar manner except that 2 moles of ethylene oxide was used per mole of 2,2' methylenebis (1,1,3,3-Tetramethylbutylphenol). Cloud point 1% aqueous <0° C.
- 15 b) 2,2' methylenebis [4-(1,1,3,3-Tetramethylbutyl)phenol] 18 EO was prepared in a similar manner except that 18 moles of ethylene oxide was used per mole methylenebis (octylphenol) in Example II. Cloud point 1%
20 aqueous 64° C.
- c) 2,2' methylenebis [4-(1,1,3,3-Tetramethylbutyl)phenol] 10 EO was prepared in a similar manner except that 10 moles of ethylene oxide was used per mole of
25 methylenebis (octylphenol). Cloud point 1% aqueous 6° C.

- 5 d) 2,2' methylenebis [4,6-di(1,1-dimethylpropyl)phenol]
16 EO was prepared in a similar manner except
that 16 moles of ethylene oxide and 2,2'
methylenebis [4,6-di(1,1-dimethylpropyl)phenol]
was used instead of 2,2' methylenebis [4-
(1,1,3,3-Tetramethylbutyl)phenol].
- 10 e) 2,2' methylenebis (4-nonylphenol) 20 EO was prepared
in a similar manner except that methylenebis
(nonylphenol) was used instead of methylenebis
(octylphenol) and 20 moles of ethylene oxide
was added per mole methylenebis (nonylphenol).
Cloud point 1% aqueous 53° C.

15 EXAMPLE III - PREPARATION OF SULFATE SODIUM SALTS

Gemini sulfate sodium salts were prepared by the
following process :

20 Ethoxylated methylene bis(octylphenol) (10 g. 8.9
mmol) was flushed with argon at 110°C for 20 minutes.
Sulfur trioxide pyridine complex dissolved in
Dimethylformamide was added to the solution at 40°C.
After temperature was brought up to 70°C, the reaction
mixture was stirred for 8 hours at this temperature.
Once TLC indicated that all starting material
25 disappeared, the reaction was slowly poured into
ice/ Na_2CO_3 water solution. The pH of solution was

maintained around 10 during the process. The reaction product was extracted twice with n-butanol. After evaporation of solvent, ethanol was added to the residue to remove inorganic salts by filtration. After
5 evaporation of alcohol in the filtrate, the leftover solid was washed with ether twice again. The final pure product was collected by filtration.

The NMR agreed with the structure.

10 EXAMPLE IV - PREPARATION OF SULFATE AMMONIUM SALTS

Gemini sulfate ammonium salts were prepared by the following process:

Ethoxylated (20EO) methylenebis(octylphenol) (24.85 g.) was bubbled with argon at 120°C for 30 minutes.
15 After temperature was cooled to 60°C, dicyandiamide (0.08 g.) was added. Stirring of the mixture was continued for another 20 minutes. Sulfamic acid (4.24 g) was added to the mixture. The reaction was stirred at 140°C for 7 hours. By that time, TLC (chloroform : methanol : water
20 = 4 : 2 : trace) showed that the starting material disappeared. The reaction was cooled to 70°C and pH adjusted to 9 by adding a small amount of monoethanolamine. The NMR agreed with the structure.

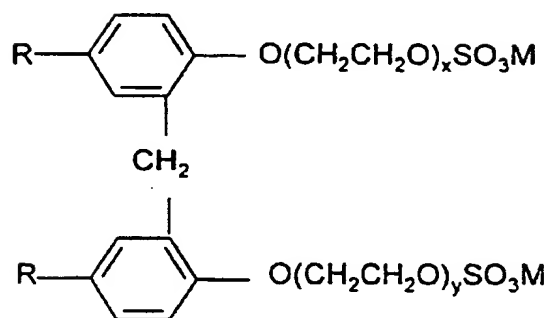
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EXAMPLE V - PREPARATION OF PHOSPHATE ESTERS

Phosphate Esters salts were prepared by the following procedure:

5 Methylenebis(octylphenol) sodium phosphate: A solution of Triethylamine (1.43 g, 14.15 mmol), methylene bis(octylphenol) (3.0g, 7.0 mmol) in dry hexane/THF was added dropwise to a solution of phosphorous oxychloride (1.30 mL, 14.15 mmol) in small amount of hexane under
10 argon at -5°C. A white precipitate appeared. After stirring 2.5 hours at 0°C, TLC (CHCl_3 : CH_3OH = 5:1) showed that all starting material disappeared, the reaction was stopped by filtered off triethylammonium chloride salt. The solvent in filtrate was evaporated under reduced
15 pressure.

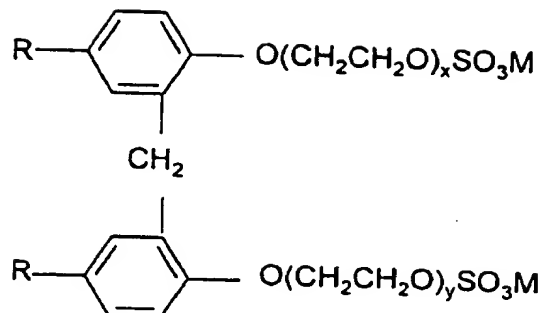
A solution of NaOH in ice water was added to the filtrate at 0°C. Final pH of the solution was about 13. The solution was stirred for two hours before it was extracted with n-butanol three times. After evaporating
20 solvent, the solid product was washed with hot ethanol to remove inorganic salt. Ethanol was evaporated under reduced pressure, and the solid was washed with cold acetone again. The final white pure product was collected by filtration. This material was confirmed by
25 ^1H -NMR, ^{13}C -NMR and P-NMR. The yield of reaction was 90%.

EXAMPLE VISURFACE ACTIVITIES

5

X+Y	R	M	Prepared by Method of Example	γ_{cmc} dyne/ cm	CMC (M)	pC ₂₀	Draves wetting 0.1% (sec)
0	C ₈ H ₁₇	Na	III	27.8	7.9×10^{-5}	5.8	5.7
2	C ₈ H ₁₇	Na	III	30.0	1.6×10^{-5}	6.1	20.6
2	C ₈ H ₁₇	NH ₄	IV	29.8	6.9×10^{-6}	6.2	30.0
18	C ₈ H ₁₇	Na	III	38.2	5.6×10^{-6}	6.3	
18	C ₈ H ₁₇	NH ₄	IV	36.0	3.4×10^{-6}	6.7	
22	C ₈ H ₁₇	NH ₄	IV	39.6	3.2×10^{-6}	6.3	

10



X+Y	R	M	Method	δ dyne/cm
0	C ₈ H ₁₇	Na	V	27.6
18	C ₈ H ₁₇	Na	V	29.1

5 The above data indicates that increased effectiveness (much lower CMC) and increased efficiency (higher pC₂₀ values) can be obtained by using the compounds of the invention.

10 EXAMPLE VII - IRRITATION

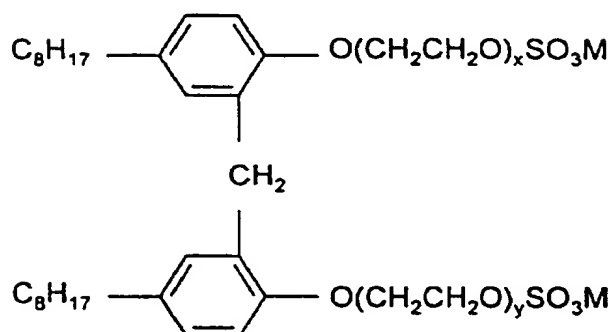
The products of this invention were evaluated for mildness by an In-Vitro Ocular Irritation (Eytex) study.

15 Alcohol sulfates and alcohol ether sulfates have eye irritancy properties which limit their use in personal care applications. Usually irritation ameliorating agents are used in combination with sulfates to minimize

irritation. Compounds of this invention at 1% level have been shown to be minimal/mild when tested by the Eytex method.

5 Eytex Draize Equivalent (EDE)

 0-15 Minimal
 15-19 Minimal/Mild
 19-22 Mild
 10 22-25 Mild/Moderate
 25-33 Moderate



15

X+Y	M	EDE
2	NH ₄	15.8
13	NH ₄	16.0
0	Na	16.2

A standard laurylether (IEO) sulfate has a score of 27.1
 20 under the same conditions.

By virtue of this property the surfactants of the invention can be used in personal care applications without the need for additional additives.

The above data indicates that increased
5 effectiveness (much lower CMC) and increased efficiency (higher pC_{20} values) can be obtained by using the compounds of the invention.

Thus when the surface properties for the compounds of the invention are compared to the corresponding
10 conventional surfactants [$C_{12}H_{25}OCH_2CH_2OSO_3Na$ has a $cmc = 4.8 \times 10^{-3}$. See E. Gotte, 3rd Int. Congr. Surface Activity, Cologne, 1, 45 (1960)] such as shown in the Table, the novel compounds of the invention show two unexpected surface active properties; unusually low critical micelle
15 concentration (CMC) and pC_{20} values in aqueous media. These properties are a measure of the tendency of the surfactant to form micelles and adsorb at the interface, and consequently, to reduce surface tension respectively.

The values shown in the Table demonstrate that the
20 compounds of Example III, IV and V are one to two orders of magnitude (10 - 100 times) more efficient at reducing surface tension. For example, the pC_{20} value for sodium lauryl ether (1EO) sulfate is 3.8. See J. A. Caskey; J. Colloid Interface Sci. 35, 46 (1971) and more than one
25 order of magnitude (or >10 times) more efficient at forming micelles. This unusually high surface activity

for these molecules is a result of their unique structure; the presence of two optimally spaced hydrophobic chains and hydrophilic groups. This molecular structure provides energetically favorable decreases in the free energy of adsorption and micellization through favorable distortion of water structure, and, at the same time, providing a "close packed" arrangement at the interface. The ability of the compounds of the invention to distort the water structure through inhibition of crystalline or liquid crystalline phase formation in bulk phase and at the same time to pack closely on adsorption at the interface is contrary to conventional wisdom. This again demonstrates the uniqueness of the molecular design for these compounds which is very critical to providing unexpected exceptional surface and performance properties.

Because of their unusually high surface activity, coupled with their hydrotropicity and solubilization properties, compounds of this invention will provide exceptionally high performance properties, at very low concentration, in practical applications such as detergency emulsification, solubilization, dispersancy, hydrotropicity, foaming and wetting. In addition, due to their extremely low monomer concentration at use levels, because of their extremely low CMC and pC_{20} values, use of one to two orders of less amounts of the compounds of the invention (compared to conventional surfactants) can

provide extremely low or no irritancy in personal care applications.

5 The unusually high surface activity of the anionic surface active agents of the invention make them the surfactants of choice in enhancing the surface activity of mixtures containing other conventional zwitterionic, amphoteric, nonionic and cationic surfactants. It has been surprisingly found that the compounds of the invention can be mixed with cationic surfactants to form
10 stable blends. This is a significant improvement in the art of forming the surfactant blends which are normal in commercial products.

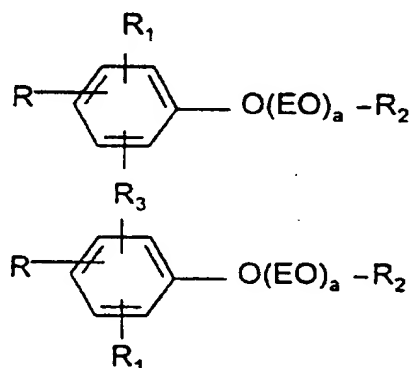
The properties of enhancement of surface activity, solubilization, and wetting of blends, even when used in
15 small concentrations, can have a wide applicability in industrial, personal care, and pharmaceutical applications where the use of the compounds of the invention, in combination with other conventional surfactants, can provide improved performance blends.

20 Although the subject invention has been described with respect to a preferred embodiment, it will be readily apparent to those having ordinary skill in the art to which the invention pertains that changes and modifications may be made thereto without departing from
25 the spirit or scope of the subject invention as defined by the appended claims.

What is claimed is:

1. Bis-alkylphenol alkoxyated gemini surfactants characterized as mild and environmentally benign comprising compounds of the formula:

I.



- wherein R independently represents alkyl of from about 4 to about 20 carbon atoms, R₁ independently represents hydrogen and alkyl of from 4 to about 20 carbon atoms; R₂ independently represents -SO₃M, -P(O)(OM)₂, -CH₂COOM, -CH₂CHOHCH₂-SO₃M, wherein M represents hydrogen, alkyl or alkaline earth metal, ammonium or an organic base salt; R₃ represents alkylene of from one to about 10 carbon atoms or -C(O)-R₄-C(O)- wherein R₄ represents alkylene of from 1 to about 10 carbon atoms or aryl.

2. The surfactants of Claim 1, wherein R independently represents straight or branch alkyl of from about 6 to about 10 carbon atoms.
- 5 3. The surfactants of Claim 1, wherein R_1 is hydrogen.
4. The surfactants of Claim 1, wherein R_2 is $-\text{SO}_3\text{M}$, $-\text{P}(\text{O})(\text{OM})_2$, CH_2COOM , and $\text{CH}_2\text{CHOHCH}_2\text{SO}_3\text{M}$.
- 10 5. Surfactants of Claim 1, wherein R_3 represents lower alkylene of from 1 to about 4 carbon atoms.
6. The surfactants of Claim 1, wherein R_3 represents $-\text{C}(\text{O})-\text{R}_4-\text{C}(\text{O})-$.
- 15 7. The surfactants of Claim 1, wherein R_4 is alkylene.
8. The surfactants of Claim 1, wherein R_4 is phenylene.
- 20 9. The surfactants of Claim 1, wherein R_2 is $-\text{SO}_3\text{M}$ or $-\text{P}(\text{O})(\text{OM})_2$.
- 25 10. The surfactants of Claim 1, wherein said organic base salt is selected from the group consisting of monoethanolamine, diethanolamine, triethanolamine,

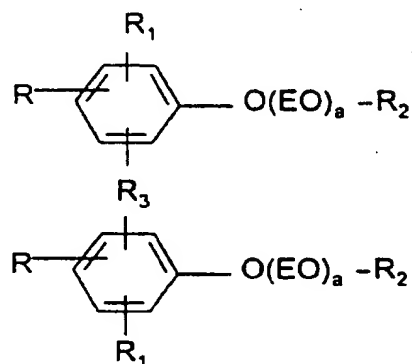
triethylamine, trimethylamine and N-hydroxyethyl morpholine.

11. The surfactants of Claim 1, wherein M in Formula I is
5 the alkali metal sodium.

12. The surfactants of claim 1, wherein said surfactant
comprises compounds of the formula:

10

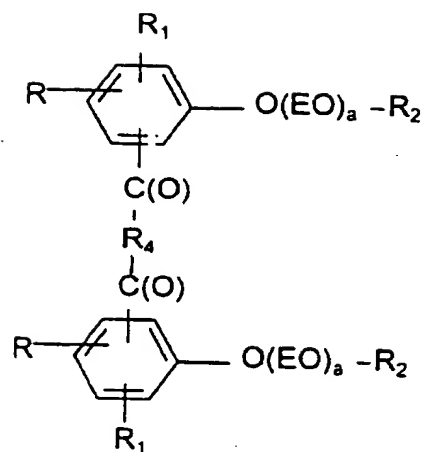
II.



15 wherein R_3 is alkylene of from 1 to about 10 carbon.

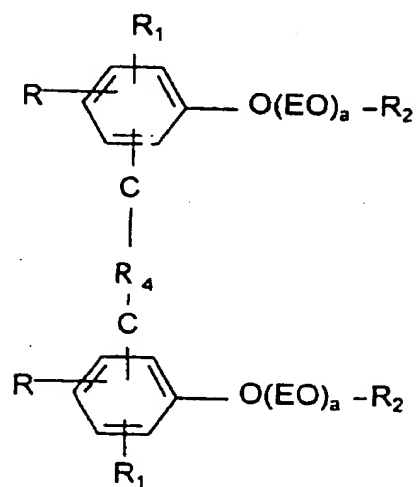
13. The surfactants of claim 1, wherein said surfactant
comprises compounds of the formula:

III.



- 5 14. The surfactants of claim 1, wherein said surfactant comprises compounds of the formula:

IV.



15. The surfactants of Claim 1, further comprising a surfactant selected from the group consisting of an anionic, nonionic, cationic, and amphoteric surfactant.
- 5
16. The blend of surfactants of Claim 15, wherein said nonionic surfactant is selected from the group consisting of a fatty acid glycerine ester, a sorbitan fatty acid ester, a sucrose fatty acid ester, a polyglycerine fatty acid ester, a higher alcohol ethylene oxide adduct, a single long chain polyoxyethylene alkyl ether, a polyoxyethylene alkyl allyl ether, a polyoxethylene lanolin alcohol, a polyoxyethylene fatty acid ester, a polyoxyethylene glycerine fatty acid, a polyoxyethylene propylene glycol fatty acid ester, a polyoxyethylene sorbitol fatty acid ester, a polyoxyethylene castor oil or hardened castor oil derivative, a polyoxyethylene lanolin derivative, a polyoxethylene fatty acid amide, a polyoxyethylene alkyl amine, an alkyl pyrrolidone, glucamides, alkylpolyglucosides, a mono or dialkanol amide, a polyoxyethylene alcohol mono or diamide, and an alkylamine oxide.
- 10
- 15
- 20
- 25 17. The blend of surfactants of Claim 15, wherein said anionic surfactant is selected from the group

consisting of a fatty acid soap, an ether carboxylic acid and salt thereof, an alkane sulfonate salt, an α -olefin sulfonate salt, a sulfonate salt of a higher fatty acid ester, a higher alcohol sulfate ester salt, fatty alcohol ether sulfate salts, a higher alcohol phosphate ester salt, a fatty alcohol ether phosphate ester salt, a condensate of higher fatty acids and amino acids, and a collagen hydrolysate derivative.

10

18. The blend of surfactants of Claim 15, wherein said cationic surfactant is selected from the group consisting of an alkyltrimethylammonium salt, a dialkyl-dimethylammonium salt, an alkyldimethylbenzylammonium salt, an alkylpyridinium salt, an alkylisoquinolinium salt, benzethonium chloride, and an acylamino acid type cationic surfactant.

15

20 19. The blend of surfactants of Claim 15, wherein said amphoteric surfactant is selected from the group consisting of an amino acid, betaine, sultaine, phosphobetaine, an imidazoline type amphoteric surfactant, soybean phospholipid, and yolk lecithin.

25

20. A cleaning composition comprising an aqueous solution having a cleaningly effective amount of the composition of Claim 1 dissolved therein.
- 5 21. The cleaning composition of claim 20, wherein the solution is selected from the group consisting of hair shampoos, baby shampoos, body shampoos, bubble baths, bar soaps, bath gels, hair conditioning gels, skin creams and lotions, skin contacting cosmetics,
10 make up removal creams and lotions, liquid detergents, dish detergents, liquid soaps, bleach activators, bleach stabilizers and the like.

INTERNATIONAL SEARCH REPORT

Int: nal Application No
PCT/IB 96/01456

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07C305/10 C07C305/06 C07F9/09 C07F9/12 C11D1/29
C11D1/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07C C07F C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 919 429 A (M. GROSSMANN, ET AL.) 11 November 1975 see column 1; example 1 ---	1-5,9, 11,12
X	GB 2 150 569 A (SANDOZ) 3 July 1985 see the whole document ---	1-5,9, 11,12,15
X	US 4 592 809 A (J.J. FONG, ET AL.) 3 June 1986 see the whole document ---	1-5,9, 11,12
P,X	EP 0 732 323 A (EXXON RESEARCH AND ENGINEERING) 18 September 1996 see the whole document ---	1-5,9, 11,12,15
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search

27 March 1997

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INTERNATIONAL SEARCH REPORT

Inter- nal Application No
PCT/IB 96/01456

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	US 4 918 211 A (K. YOKOTA, ET AL.) 17 April 1990 see the whole document ---	1,15
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information on patent family members

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